

Density functional calculations of planar DNA base-pairs

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We present a systematic Density Functional Theory (DFT) study of geometries and energies of the nucleic acid DNA bases (guanine, adenine, cytosine and thymine) and 30 different DNA base-pairs. We use a recently developed linear-scaling DFT scheme, which is specially suited for systems with large numbers of atoms. As a first step towards the study of large DNA systems, in this work: (i) We establish the reliability of the approximations of our method (including pseudopotentials and basis sets) for the description of the hydrogen-bonded base pairs, by comparing our results with those of former calculations. We show that the interaction energies at Hartree-Fock geometries are in very good agreement with those of second order Møller-Plesset (MP2) perturbation theory (the most accurate technique that can be applied at present for system of the sizes of the base-pairs). (ii) We perform DFT structural optimizations for the 30 different DNA base-pairs, only three of which had been previously studied with DFT. Our results provide information on the effect of correlation on the structure of the other 27 base pairs, for which only Hartree-Fock geometries were formerly available.

I. INTRODUCTION

Hydrogen bonds between complementary purine-pyrimidine bases play a significant role in the bonding between the two strands of the double helix structures of DNA¹. Nevertheless, other factors are also of paramount importance in determining the structure of the helix. For instance, base-stacking²⁻⁴ plays a crucial role in preserving the hydrophobe aromatic rings from interacting with water molecules, besides contributing to increase the Van der Waals interactions. Also, both counterions^{5,6} and water molecules are important in screening the electrostatic repulsion between the negatively charged phosphate groups. The theoretical study of these systems and the effects of each type of interaction have been hindered by the great complexity of the calculations, both due to the difficulty in treating such different interactions, and to the large number of atoms involved.

Although some progress has been done recently,⁷ semi-empirical quantum chemistry (QC) methods and empirical force fields^{8,9} are generally not accurate enough to describe these systems. The most reliable procedure is undoubtedly the *ab-initio* QC approach, in which the accuracy of the calculation can be systematically improved by increasing the size and quality of the basis set and the level of correlation included¹⁰. This can be a powerful method to study DNA and other biological systems, and a unique tool to address some of their properties. However, the intensive numerical effort required by these methods poses a serious limitation to the system sizes

that can be handled at a satisfactory level of the theory¹⁰, a fact which has precluded their use in realistic biological systems.

An alternative, which allows calculations for system sizes well beyond the limits of the traditional *ab-initio* QC methods, is the Density Functional Theory^{11,12} (DFT). At present, it appears that DFT is the only first principles method potentially capable of handling the large sizes involved, although the standard DFT techniques are still too expensive to solve systems with more than a very few hundreds of atoms, like those in DNA molecules. If the DFT methods are to make an impact in biological systems, it is necessary to be able to go beyond the current size limits, but maintaining the current accuracy. In this context, an extremely promising development has been the recent search for computational techniques in which the numerical effort scales only linearly with system size: the so called 'order-N' methods (see Ref. 13 for a review). They open, for the first time, the possibility of performing calculations in very large molecules, and have already been applied to the study of DNA chains with many hundreds of atoms by means of semi-empirical Hamiltonians¹⁴ and approximate, non-selfconsistent DFT¹⁵.

The application of order-N techniques in the context of fully first-principles, selfconsistent DFT calculations is, in general, in a less advanced development state. Nevertheless, we have recently proposed a DFT method and the corresponding computer code SIESTA, with order-N scaling, which is able to do such calculations in systems

with thousands of atoms, in single-processor workstations^{16–19}. Our preliminary tests^{17,18} have demonstrated that the method is able to treat systems as large as a whole turn of a DNA chain with more than 650 atoms, therefore opening the possibility of studying large biological molecules from first principles. Work in this direction is underway, and will be published elsewhere.²⁰

The purpose of this paper, as a first step in the application of the method to complex biological systems, and in particular to DNA molecules, is to make a thorough study of isolated nitrogenated bases and hydrogen-bonded base-pairs. This study serves to validate the present method (basis orbitals, approximations and numerical techniques) for the study of these base-pairs, by comparing the energies and geometries with those of previous calculations, where available. The results presented here show that our method provides a very accurate description of these systems, with the advantage of being considerably fast and, as mentioned, capable of reaching very large system sizes. Besides, we provide a systematic DFT study of the structures of the different base-pairs, and the effect of the relaxations on the interaction energies. The use of our DFT scheme to obtain equilibrium geometries has the advantage that it includes correlation effects, which are absent in the available Hartree-Fock (HF) geometries.²¹ At the same time, it is computationally feasible, unlike the Møller-Plesset second order perturbation theory²² (MP2) method.

The rest of this paper is organized as follows. In Section II we discuss the details of our DFT method and of the calculations performed. Section III describes the energetics of the base-pairs at the available HF geometries, comparing our results with those of MP2 calculations in the literature. Section IV presents our results for the DFT structural relaxations. Finally, in Section V we present the conclusions of this work.

II. METHOD AND CALCULATIONS DETAILS

A. The SIESTA method

All our calculations have been done with SIESTA¹⁸, a code for DFT calculations in systems with a large number of atoms, in which the cost of the calculation (both in memory and CPU time) scales linearly with the size of the system. Here we give only a brief description of the basic approximations involved in the calculation, whereas a detailed description can be found in Refs. 18,19.

We treat exchange-correlation (XC) within the framework of the Kohn-Sham formulation¹² of DFT¹¹. It is rather well known from many calculations in a variety of systems^{23–27} that a correct description of hydrogen-bonds requires the use of non-local XC functionals. The Local Density Approximation (LDA) yields bond distances in the hydrogen bonds which are about 10–15% shorter and binding energies about 50–70% larger than

the experimental values. Inclusion of gradient corrections in several Generalized Gradient Approximations (GGA) functionals improves the description dramatically, achieving levels of accuracy an order of magnitude better than LDA. In this work we have used the first principles GGA functional proposed recently by Perdew, Burke and Ernzerhof²⁸ (PBE).

SIESTA uses non-local, norm-conserving pseudopotentials to eliminate the core electrons from the calculation, and to produce a smoother valence charge density. In this work, the pseudopotentials are obtained from first principles, following the scheme of Troullier and Martins²⁹. The valence electrons are described using the linear combination of atomic orbitals (LCAO) approximation.

An essential ingredient for the linear scaling within this approach is the finite range of the matrix elements between atomic orbitals. To achieve it, we use basis orbitals which strictly vanish beyond a cutoff radius³⁰ (instead of the usual approach of using decaying orbitals and neglecting matrix elements by whatever criterion). The main advantage is consistency: given a basis, the eigenvalue problem is solved for the *full* Hamiltonian. Thus, the procedure is numerically very stable even for short ranges, in contrast with the usual approach. Since the computational load grows substantially with the basis range, it is important to work with basis functions that display fast convergence for short orbital ranges. We have developed a scheme for finite range basis set generation which we will now outline.¹⁹

In this and previous works, the radial parts of the finite-range orbitals were determined in the spirit of the method of Sankey and Niklewski,³¹ who proposed a scheme for minimal (single- ζ) bases that we have generalized to arbitrarily complete sets. The single- ζ orbitals are obtained by solving the DFT atomic problem (including the pseudopotential) with the boundary condition for the orbitals of being zero beyond the cutoff radius, while remaining continuous. For the efficient generation of larger, more complete basis sets we have used the ideas developed within the QC community over the years, incorporating them into new schemes adapted to numerical, finite-range bases for linear scaling. Numerical multiple- ζ bases are constructed in the split-valence philosophy^{18,19}. Given an atomic orbital, it is split into two or more functions. The first splitting is made by introducing a smooth function that reproduces exactly the tail of the original orbital beyond a specified radius. The difference between the original orbital and this smooth function is an orbital with an even shorter range. Multiple splits are obtained by repeating the procedure. Our approach also allows polarization orbitals¹⁹. These are obtained by numerically solving the problem of the isolated atom in the presence of a polarizing electric field. Comparing the solution with a perturbative expansion (Sternheimer equations³²) gives the shape of the wanted polarization orbitals. The cutoff radius of the polarization orbitals is therefore the same as the one of the shell being polarized.

In all the calculations presented in this work we have used a double- ζ (split valence) basis with polarization functions in all the atoms (including hydrogen). The cutoff radii for the atomic orbitals of each element can be seen in Table I, as were obtained by fixing a confinement energy³⁰ of 50 meV.

The matrix elements of the different terms of the Kohn-Sham Hamiltonian are calculated in one of two different ways¹⁸. The terms that involve integrals over two atoms only (kinetic energy, overlap, and other terms related with the pseudopotential, see below) are computed a priori as a function of the distance between the centers, and stored in tables to be interpolated later with very little use of time and memory. The other terms are calculated with the help of a uniform grid of points in real space. The smoothness of the integrands determines how fine a grid is needed, and, of course, the finer the grid, the more expensive the calculation. We remark that the use of pseudopotentials, which eliminates the rapidly varying core charge, is essential to provide functions smooth enough to make the grid integration feasible. This fineness is measured by the energy of the shortest wave-length plane-wave that can be described with the grid, in analogy with plane-wave calculations. In all the calculations presented here, we have used a cutoff of 125 Ry.

The calculation of the pseudopotential matrix elements is done very efficiently using the Kleinman-Bylander³³ factorized form. It allows the three-center integrals of the pseudopotential between atomic orbitals to be treated as products of two-center integrals, which are tabulated as described above.

With the bases, approximations and techniques described so far, the Kohn-Sham hamiltonian is built up with order-N operations. The solution to the eigenvalue problem can also be obtained with a linear scaling effort using techniques recently developed, and available in SIESTA^{13,34}. For the small systems considered here, however, the straight diagonalization (which scales as the cube of the number of orbitals) requires very little effort, and therefore has been used in this work to solve the Kohn-Sham eigenvalue equations.

B. Details of the calculations

In order to reach reliable conclusions about the accuracy of our method, we have used in this study a large set of 30 base-pairs. Besides the common Watson-Crick guanine-cytosine and thymine-adenine pairs, we also consider a significant range of other configurations of the four bases guanine, cytosine, adenine and thymine (G, C, A, T). These are the same as those studied by Šponer *et al.*²¹ in their MP2 study. The Watson-Crick configurations are designated WC, and the Hoogsteen, reversed Hoogsteen and reversed Watson-Crick appear as H, RH, RWC respectively. Other configurations are distinguished simply

with numbers, eg. AA1, AA2, etc. In assigning the numbers to the pairs we have followed the nomenclature of Hobza and Sandorfy³⁵, who classified the pairs in order of decreasing stability. Their ordering was not confirmed by later results (including ours), but the convention is nevertheless maintained to simplify comparisons and avoid confusion. The structures of the bases and base-pairs studied in this work can be found in Figures 1 and 2 of Ref. 21. For the numbering of the atoms we followed Ref. 36.

In the calculation of the energetics of the base-pairs, we have analyzed two different quantities. First, the interaction energy E_{int} , defined as the energy of the base-pair minus the energy of each base with the same geometry it has in the pair. Second, the total stabilization energy, E_t , defined as the difference between the energy of the pair and that of each base in its isolated optimal geometry. Therefore, the difference between E_t and E_{int} is the deformation energy, *i.e.*, the increase in intramolecular energy due to the geometry change when the base-pair is formed.

Due to the finite size of the bases used, both E_{int} and E_t have to be corrected for the basis set superposition error³⁷ (BSSE). In this work, all the energies have been corrected for BSSE, as described in the following. For the interaction energy, we have used the standard Boys-Bernardi counterpoise correction³⁷: the BSSE is calculated as the difference between the energies of the isolated bases obtained with the orbitals of the base alone, and with the “ghost” orbitals of the other base: $BSSE = E(A) + E(B) - E(A*) - E(B*)$ (where the asterisks indicate the inclusion of the orbitals of the other base in the calculation). The same correction is used for the stabilization energy E_t . Since E_t contains the deformation energy E_{def} , this approach is valid only if E_{def} is not much affected by the BSSE (*i.e.*, if the change in the BSSE is not large when calculated with the relaxed isolated bases geometry instead of the coordinates of each base in the pair)³⁸. We tested this and found that the variation in BSSE calculated with these two geometries is only about 10% of the total BSSE value, so we will consider that the BSSE correction defined above is as valid for E_t as for E_{int} .

The structural relaxations were done by means of a conjugate gradient minimization of the energy, until the forces on all atoms were smaller than 0.04 eV/Å. No constraints were imposed in the relaxation, except the planarity of the base-pairs. This constraint was imposed in order to facilitate comparison with the results of Šponer *et al.*, who also analyze planar bases and base-pairs. In the relaxations, forces are calculated as analytical derivatives of the total energy¹⁸. No BSSE correction was included in the forces. This would lead to problems if the BSSE had an important variation with atomic positions, since in that case the relaxed geometries obtained without the BSSE correction would not correspond to the minimum of the total energy including the BSSE correction. In order to check this, corrected and not corrected

interaction energies of the AA1 base-pair were calculated as a function of the distance, separating the molecules rigidly in the H bonds direction. As expected, the BSSE is more important in absolute value as the two bases are brought closer, and decreases as the bases are separated. However, the results show that this variation does not appreciably affect neither the equilibrium distance (the acceptor-hydrogen distance was 1.95 Å for the uncorrected curve and 1.97 Å for the corrected one) nor the vibrational frequencies.

Finally, it is worth mentioning the computational requirements of the calculations presented here. All the computations were performed in a PC with a 120 MHz Pentium processor. For the relaxations of the base-pairs, the calculations took an average of about 4 hours of CPU time for each relaxation step. The memory usage was below 100 Mb, and virtually no disk use was necessary (all the integrals being stored in memory). This shows the efficiency of the code, and the possibility of studying relatively large systems in very modest platforms.

III. ENERGIES AT HF/6-31G** GEOMETRIES

In order to demonstrate the accuracy and validity of our method for the description of the energies of hydrogen-bonded base-pairs, we need a reference with which to compare our results. Since the experimental information on energies and structures of isolated bases and base-pairs is very scarce, we have used the results from former *ab-initio* calculations as a benchmark. There is a large amount of work done in these systems in the context of *ab-initio* QC methods.¹⁰ Probably the most complete and sophisticated calculations are those performed by Šponer and coworkers,²¹ using the MP2 method. This usually covers a substantial part of the correlation energy, and is the most accurate correlation technique that can be applied at present for systems of the size of a few tens of atoms, like the base-pairs. However, these calculations are still computationally expensive, and therefore they can only be done using medium sized bases (typically 6-31G**) and fixed geometries obtained with simpler schemes like HF. Geometry optimizations at the MP2 level have only been possible for the smallest, highest symmetry base-pair (cytosine-cytosine)²¹.

We will therefore discuss the interaction energies obtained with SIESTA for the base-pairs in the HF/6-31G** geometries of Šponer *et al.*²¹, and compare with the corresponding MP2 results. The data are shown in Table II. GG2 and GC2 base-pairs are not included in this table because at this level of relaxations these pairs are not stable and converge to the configurations of GG1 and GCNEW, respectively. We compare with the MP2 results²¹ evaluated on the same geometry. We also show the percentage deviation between both results. For all the base-pairs except GG4, the agreement is considerably good, with differences smaller than 8% and much

less in most cases. GG4 seems to be an exception to the general trend as its difference with the MP2 value is 26%. We tried to see if this was a problem of the basis set and made calculations with larger cut-off radii for the atomic orbitals. For an energy shift of 10 meV the interaction energy was -8.4 kcal/mol, so the deviation with respect to the MP2 results is reduced to 16%, but it is still far larger than for the rest of the base-pairs (for other base-pairs, the difference in the interaction energy for the 50 and 10 meV energy shift bases is much smaller than in the GG4 case).

The standard deviation of our results compared to the MP2 values is of 0.73 kcal/mol. It is interesting to compare these results with the DFT values obtained by Šponer *et al.*²¹ for the same HF/6-31G** geometries, using the Becke3LYP functional³⁹. The largest deviation of their results is of 1.3 kcal/mol (11 % of E_{int}) for the TC1 pair, while the standard deviation from the MP2 results is accidentally the same as ours: 0.73 kcal/mol. We can therefore conclude that the results obtained for the energies at fixed geometries using the PBE functional are of similar degree of accuracy as those obtained by other authors with other GGA functionals. The standard deviation between our results and the DFT data of Šponer *et al.* is about 0.85 kcal/mol, of the same order as the difference with the MP2 results. This serves to validate the PBE functional, as well as SIESTA and the approximations involved (cut-off bases, pseudopotentials, grid integrations, etc), as a valuable and competitive tool compared with standard, all-electron, gaussian-bases DFT programs.

The current LDA and GGA implementations of DFT are not able to describe accurately Van der Waals or dispersion interactions. Still, the previous results show that the common non-local XC functionals provide quantitatively accurate values of the interaction energies of the hydrogen-bonded base-pairs. Although the reason for this is not fully clear yet, it seems that the dispersion energies in these H-bonded systems are significantly smaller than the ones that would be predicted using an empirical London dispersion energy²¹. It is still unclear if current XC functionals are able to describe the interaction between stacked base-pairs, where the dispersion energy is larger than expected from an empirical London formula. Calculations by Šponer and coworkers⁴ seem to indicate that the Becke3LYP functional significantly underestimates the dispersion energies for stacked base pairs. A study of the performance of other XC functionals with our method is underway, and will help in clarifying this issue.

To conclude this section, we show in Table III the dipole moments for the HF/6-31G** geometries. We compare the results of the HF/6-31G** calculations of Šponer *et al.*²¹ with those of this work. DFT provides lower values, due to the tendency of the Hartree-Fock approximation to overestimate the electrostatic interactions.

IV. DFT GEOMETRY OPTIMIZATIONS

At present, DFT studies of the geometries of base-pairs are rather scarce. To our knowledge, only the geometries of the Watson-Crick TA and GC, and the CC base-pairs have been obtained with DFT. Therefore, we have extended the previous DFT works, and performed a thorough study of the energetics and structural relaxations of nitrogenated base-pairs with our DFT approach. Here we describe the results of such structural optimizations for the 30 hydrogen-bonded base-pairs (27 of which had not been studied with DFT previously).

A. Isolated bases

We have first optimized the geometries of isolated adenine, guanine, cytosine and thymine using our method. The results for the geometries obtained (bond distances and angles) are presented in Tables IV-VII. For comparison, we also show the DFT results of Santamaría and Vázquez²⁷ (S-V), obtained with the Vosko-Wilk-Nusair⁴⁰ functional with Becke-Perdew⁴¹ non-local corrections, as well as the experimental values obtained with X-ray diffraction for crystallized DNA^{42,43}. The bases were relaxed for planar geometries.

We can observe that the geometries obtained here are close to those of S-V with an all-electron calculation with gaussian bases and a different XC functional. Again, this supports the reliability of SIESTA and its approximations. The bond distances obtained in this work are usually slightly larger than the values of S-V, although the largest difference is only 0.016 Å. The results of S-V are slightly closer to the experimental data. These must be taken only as a rough reference, since they correspond to measurements of DNA crystals; packing forces constrain the molecules, so all the bond distances are shorter than those calculated for the free bases. Some of the differences between our results and those of S-V are due to the restriction of planarity in our calculation, which was not imposed by S-V. It is well known that the amino groups of the nucleic acid bases suffer a pyramidalization due to partial sp^3 hybridization^{10,36}: the two H atoms go out of the plane of the aromatic ring whereas the N atom moves in the opposite direction. Therefore, there are in some cases important differences in the distances and angles that involve atoms in the amino groups of the bases between the planar and non-planar bases.

B. Base-pairs

Here we discuss our results for the structural optimizations of the base-pairs performed with the SIESTA program. Our relaxations start from HF/6-31G** geometries, with the exception of GG2 and GC2 base-pairs, (not stable at the HF/6-31G** level) for which we start

from the HF/MINI-1 coordinates. In all cases, planar symmetry was imposed in the relaxations.

Table VIII shows the H-bonds distances and angles for the base-pairs obtained with our method. Donor-acceptor and donor-hydrogen distances are shown, together with the angle subtended by the three atoms involved in the bond. Comparing with HF/6-31G** geometries (see Ref. 21), we see that hydrogen bridges are shorter and donor-H distances are larger in our calculations.

Among the hydrogen bonds in the base-pairs studied, 33 are $N(H)\cdots N$ and 29 are $O\cdots(H)N$. Their distances range from 2.755 to 3.169 Å. Among the longest of them, there is a clear majority of $N(H)\cdots N$, which seems logical because the electrostatic attraction between the H atom and a N atom should be weaker than the attraction between H and O. However, there are also some $N(H)\cdots O$ bonds that are quite long. The reason is that several factors and interactions, and not only the atoms which are involved in the H-bond, influence the final configuration of the pairs.

Distances between donor and H atoms range from 1.026 to 1.070 Å. There is in many cases a correlation between short H-bond distances and long donor-H distances. It is clear that the greater the electrostatic attraction the H atom suffers from the other base, the longer will be its distance from the donor atom and vice-versa. However, again this cannot be taken as a strict rule, as the final position of each atom is determined by all the neighboring atoms.

The dipole moments at the geometries relaxed with our approach are shown in Table III. They are all smaller than the HF/6-31G** values, except for two of the bases, and there are no major differences with the results obtained with SIESTA for the HF/6-31G** geometries, although there is in almost all cases a slight increase in their values.

Table IX shows the interaction (E_{int}) and total stabilization (E_T) energies for the base-pairs, obtained at the SIESTA relaxed coordinates. The ordering of the base-pairs is the same as the one of Table II, to facilitate comparison. Interaction energies range from -32.2 to -9.6 kcal/mol, and stabilization energies from -27.7 to -8.0 kcal/mol. The most stable base-pair is GCWC, in agreement with previous results^{21,35}, and the ordering of the next three base-pairs is also the same. The relative ordering (according to E_{int}) of all the TA, GT, GG, GA, AA and TT tautomers is conserved, but AC2 is more stable than AC1 and TC2 more stable than TC1 with our method. It is interesting to see that the energetic ordering depends on which of the two energies is used, E_{int} or E_t . This is not the case in MP2//HF results²¹, where only two base-pairs change position when ordered according to E_{int} instead of E_t (although the ordering could change further if the geometries were obtained at the MP2 level, too).

Several points are worth noticing from the results of Table IX. (i) The interaction energies are systematically

larger (by a few kcal/mol) than those obtained, with the same theory, at the HF/6-31G** geometries (compare with the results of Table II). This indicates that the geometry of the H-bonded base-pairs configurations are more sensitive to the details of the calculation than those of the free bases, and that the HF/6-31G** geometries for the H-bonds are not fully optimal for DFT calculations. (ii) The deformation energies (difference between E_T and E_{int}) are larger than those obtained at the HF/6-31G** and MP2 levels for HF/6-31G** geometries. In our calculations, the deformation energy ranges up to as much as 6.7 kcal/mol for the GCNEW pair. The same trend is observed in other DFT calculations (see below). (iii) The GG2 and GC2 base-pairs, which at the HF/6-31G** are unstable and converge towards the GG1 and GCNEW respectively, are found to be stable in our geometry optimization, which was started from HF/MINI-1 coordinates. The interaction energy of these pairs is small, but comparable to many of the other base-pairs.

To our knowledge, DFT optimizations of base-pairs by other authors are only available for GCWC, TAWC and CC^{21,27}. Tables X, XI and XII present the available DFT results together with those of SIESTA and HF/6-31G**, for these three pairs. For CC, results of a MP2 geometry optimization are also available from the work of Šponer *et al.*²¹, and are included in Table XII. Acceptor-donor and donor-hydrogen distances are shown, together with the interaction and stabilization energies. In general, our results report donor-acceptor distances which are only slightly shorter than those of other DFT calculations (with a maximum difference of 0.058 Å), whereas the donor-H distances are in excellent agreement. All DFT results yield shorter D-A distances than the HF/6-31G** approximation. For the energies, the dispersion in the DFT reports is considerable. Our results agree quite well with those of Šponer *et al.*²¹ (available for GCWC and CC), whereas the differences with those of Santamaría and Vázquez²⁷ (available for GCWC and TAWC) are larger. We note that, as mentioned before, deformation energies are considerably larger in all the DFT results than in the MP2//HF results. For instance, for GCWC, the DFT calculations yield values of the deformation energies of 3.3, 4.8 and 4.7 kcal/mol, whereas the MP2//HF result is of only 2.1 kcal/mol.

It is interesting to discuss the case of CC, since it is the only base-pair where coordinates optimizations at the MP2 level are available. We see in Table XII that the bond length between the donor and acceptor atoms is underestimated by the DFT calculations, and overestimated by the HF/6-31G** by about the same amount. However, it seems that the DFT energies are closer to the MP2 values at the MP2 geometries than at the HF ones. Also, the MP2 deformation energy increases from 1.3 kcal/mol for the HF/6-31G** geometries to 1.8 kcal/mol for the MP2 geometries, and therefore approaching that obtained with DFT (2.3 kcal/mol in the results of Šponer *et al.* and 2.4 kcal/mol in our case).

V. CONCLUSIONS

In this work, we have performed DFT calculations on the DNA bases adenine, guanine, cytosine and thymine, and 30 base-pairs formed by these bases. The calculations were performed with the SIESTA code, which is a novel technique for DFT calculations in systems with large numbers of atoms using pseudopotentials to describe the effect of the core electrons and finite range basis orbitals for the valence electrons. The calculations presented here serve to validate our method for the study of H-bonded base-pairs, as a first step toward the complete DNA helix (which is feasible with SIESTA due to the linear scaling of the numerical effort with the number of atoms in the system).

For calculations on the HF/6-31G** geometries, excellent agreement with MP2 results was obtained. The deviations are smaller than 8% (which amounts to 1.3 kcal/mol at most), except for GG4, which differs quite significantly from MP2 results. Calculations with longer atomic orbital radii reduce the difference, but it is still bigger than the rest. The dipole moments for these geometries are systematically lower than those of the HF calculations.

For the isolated bases, the planar geometries obtained in our calculation are in good agreement with former DFT results.

The relaxed geometries of the 30 DNA base-pairs were also obtained with our method. The donor-acceptor distances in the hydrogen bonds are systematically shorter than those of HF/6-31G**, as in other DFT calculations^{27,21}. Our results compare well with other DFT optimizations of the GCWC and TAWC base-pairs. For the CC pair, for which MP2 optimizations are available, the results of SIESTA and other DFT calculations slightly underestimate the hydrogen bond distances, but provide a quite accurate value for the interaction energies. The deformation energies upon the dimer formation are larger for the DFT results than for the HF geometries, a result that is in agreement with the increase of E_{def} in the MP2 approximation when MP2 coordinates are used in the calculation.

Dipole moments for the relaxed geometries are quite similar to our previous results for HF geometries, but slightly larger in most cases.

The results for the energetic ordering of the base-pairs have also been analyzed. Although there are not essential changes, the ordering is slightly different than for the MP2//HF results. However, the relative order between tautomers is conserved in most cases. The GG2 and GC2 base-pairs, which were unstable at the HF/6-31G** level, are stable in our calculations, and have interaction energies similar to the other base-pairs.

In conclusion, the results presented here show that SIESTA is a valuable tool for the study of H-bonded DNA base-pairs. It provides results very similar to other DFT techniques, and which compare very well with the avail-

able MP2 data. Work is under progress to determine the validity of the method for the properties of stacked bases, and for the study of large DNA segments.

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TABLE I. Atomic Orbitals radii (Bohr) for an energy shift of 50 meV. For each L shell, ζ stands for each of the split valence orbitals.

Species	L= 0		L= 1	
	$\zeta=1$	$\zeta=2$	$\zeta=1$	$\zeta=2$
H	6.047	2.488		
C	4.994	3.475	6.254	3.746
N	4.390	2.942	5.496	3.092
O	3.937	2.542	4.931	2.672

TABLE II. Base-pair Interaction Energies (E_{int} , in kcal/mol) at HF/6-31G** geometries.

Pair	MP2 ^a	SIESTA	Deviation (%)
GCWC	-25.8	-26.8	-3.9
GG1	-24.7	-25.1	-1.6
GCNEW	-22.2	-21.7	2.2
CC	-18.8	-17.5	6.9
GG3	-17.8	-16.6	6.7
GA1	-15.2	-15.5	-2.0
GT1	-15.1	-15.0	0.7
GT2	-14.7	-14.5	1.4
AC1	-14.3	-14.0	2.1
GC1	-14.3	-14.7	-2.8
AC2	-14.1	-14.7	-4.2
GA3	-13.8	-13.8	0.0
TAH	-13.3	-13.7	-3.0
TARH	-13.2	-13.6	-3.0
TAWC	-12.4	-12.3	0.8
TARWC	-12.4	-12.3	0.8
AA1	-11.5	-11.7	-1.7
GA4	-11.4	-11.7	-2.6
TC2	-11.6	-10.8	7.5
TC1	-11.4	-10.6	7.0
AA2	-11.0	-11.4	-3.6
TT2	-10.6	-9.9	6.6
TT1	-10.6	-10.1	4.7
TT3	-10.6	-10.2	3.8
GA2	-10.3	-10.6	-2.9
GG4	-10.0	-7.4	26.0
AA3	-9.8	-9.8	0.0
2aminoAT	-15.1	-15.2	-0.7

^a From ref. 21

TABLE III. Dipole moments (Debyes) of the DNA base-pairs^a

Pair	HF//HF	SIESTA//HF	Difference (%)	SIESTA
GCWC	6.5	5.8	-10.8	6.1
GG1	0.0	0.0	0.0	0.0
GCNEW	3.1	3.4	9.7	3.3
CC	0.0	0.0	0.0	0.0
GG3	10.5	10.3	-1.9	10.9
GA1	5.6	4.7	-16.1	4.9
GT1	7.7	6.9	-10.4	7.0
GT2	8.6	8.0	-7.4	8.3
AC1	4.8	3.5	-14.6	3.7
GC1	12.7	10.7	-15.7	11.5
AC2	9.7	8.3	-14.4	8.6
GA3	8.8	7.9	-10.2	8.4
TAH	6.4	5.5	-14.1	5.7
TARH	5.9	5.0	-15.2	5.0
TAWC	2.0	1.4	-30.0	1.4
TARWC	2.5	2.3	-8.0	2.4
AA1	0.0	0.0	0.0	0.0
GA4	9.2	8.2	-10.9	8.8
TC2	4.5	3.9	-13.3	3.8
TC1	5.9	5.3	-10.2	5.5
AA2	4.9	4.7	-4.1	4.8
TT2	0.0	0.0	0.0	0.0
TT1	1.3	1.3	0.0	1.6
TT3	0.0	0.0	0.0	0.0
GA2	7.3	6.4	-12.3	6.8
GG4	0.0	0.0	0.0	0.0
AA3	0.0	0.0	0.0	0.0
2aminoAT	4.2	4.0	-4.7	4.2
GG2	—	—	—	12.7
GC2	—	—	—	13.8

^a HF//HF: Hartree-Fock results obtained at HF/6-31G** coordinates. From ref. 21.

SIESTA//HF: results of this work, obtained at HF/6-31G** geometries.

Difference: Percent difference between HF//HF and SIESTA//HF results.

SIESTA: results of this work, calculated at the SIESTA relaxed coordinates.

TABLE IV. Bond distances and angles for isolated adenine^a.

Distances (Å)	This work	Ref. 27	Exp.	Angles (deg)	This Work	Ref. 27	Exp.
C8-N9	1.391	1.387	1.367	C8-N9-C4	107.30	106.74	105.9
N9-C4	1.390	1.386	1.376	N9-C4-C5	103.67	104.50	105.7
C5-N7	1.394	1.394	1.385	C5-N7-C8	103.35	103.75	103.9
N7-C8	1.334	1.324	1.312	N7-C8-N9	113.40	113.49	113.8
C4-N3	1.355	1.349	1.342	C5-C4-N3	127.53	126.98	126.9
N3-C2	1.357	1.348	1.332	C4-N3-C2	110.66	110.82	110.8
C2-N1	1.362	1.354	1.338	N3-C2-N1	129.26	129.21	129.0
N1-C6	1.360	1.355	1.349	C2-N1-C6	117.92	118.07	118.8
C6-N6	1.368	1.371	1.337	C5-C6-N6	121.14	122.33	123.4
C6-C5	1.431	1.418	1.409	N1-C6-C5	119.51	118.96	117.6
C4-C5	1.420	1.409	1.382	C4-C5-N7	112.28	111.52	110.7
C8-H8	1.098	1.093		N7-C8-H8	125.17	125.00	
C2-H2	1.108	1.098		N3-C2-H2	115.52	115.58	
N9-H9	1.017	1.022		C8-N9-H9	127.31	127.64	
N6-H61	1.020	1.020		C6-N6-H61	118.87	116.04	
N6-H62	1.021	1.020		C6-N6-H62	119.52	117.56	

^a This work: DFT geometries obtained with SIESTA, using the PBE²⁸ functional; Ref. 27: geometries obtained by Santamaría and Vazquez using the VWN⁴⁰ functional with BP⁴¹ non-local corrections; Exp.: experimental values from crystallized DNA (refs. 42 and 43).

TABLE V. Bond distances and angles for isolated guanine^a.

Distances (Å)	This work	Ref. 27	Exp.	Angles (deg)	This work	Ref. 27	Exp.
C2-N1	1.382	1.379	1.375	C2-N1-C6	126.77	126.68	124.9
N1-C6	1.449	1.448	1.393	N1-C6-C5	109.40	109.50	111.7
C4-N3	1.371	1.366	1.355	C4-N3-C2	111.66	112.24	111.8
N3-C2	1.335	1.324	1.327	N3-C2-N1	124.17	123.52	124.0
C2-N2	1.378	1.391	1.341	N1-C2-N2	116.83	117.2	116.3
C4-N9	1.386	1.380	1.377	C4-N9-C8	106.72	106.73	106.0
N9-C8	1.398	1.392	1.374	N9-C8-N7	113.20	112.85	113.5
C8-N7	1.329	1.321	1.304	C8-N7-C5	104.19	104.49	104.2
N7-C5	1.391	1.389	1.389	N7-C5-C4	111.31	111.01	110.8
C6-C5	1.460	1.446	1.415	C6-C5-C4	118.39	118.53	119.1
C5-C4	1.423	1.407	1.377	C5-C4-N3	129.61	129.51	128.4
C6-O6	1.237	1.234	1.239	C5-C6-O6	131.48	131.46	128.3
N1-H1	1.025	1.025		C2-N1-H1	120.11	120.06	
N2-H21	1.016	1.023		C2-N2-H22	117.27	112.9	
N2-H22	1.017	1.023		C2-N2-H21	122.36	116.37	
C8-H8	1.098	1.092		N7-C8-H8	124.76	125.32	
N9-H9	1.025	1.022		C8-N9-H9	127.56	128.11	

^a Same as in Table IV.

TABLE VI. Bond distances and angles for isolated cytosine^a.

Distances (Å)	This work	Ref. 27	Exp.	Angles (deg)	This work	Ref. 27	Exp.
N3-C2	1.386	1.379	1.356	N3-C2-N1	116.77	116.47	118.9
C2-N1	1.444	1.439	1.399	C2-N1-C6	123.38	123.38	120.6
N1-C6	1.366	1.363	1.364	N1-C6-C5	119.91	119.71	121.0
C4-N3	1.341	1.332	1.334	C4-N3-C2	119.73	119.76	120.0
C4-N4	1.374	1.378	1.337	N4-C4-N3	116.72	116.57	117.9
C6-C5	1.385	1.371	1.337	C6-C5-C4	115.87	116.18	117.6
C5-C4	1.456	1.445	1.426	C5-C4-N3	124.33	124.43	121.8
C2-O2	1.240	1.236	1.237	N3-C2-O2	125.52	125.68	121.9
N4-H41	1.020	1.019		H41-N4-H42	120.31	116.37	
N4-H42	1.023	1.022		C4-N4-H42	118.29	114.91	
N1-H1	1.027	1.023		C2-N1-H1	115.13	115.23	
C5-H5	1.100	1.094		C4-C5-H5	122.99	122.62	
C6-H6	1.101	1.096		N1-C6-H6	117.23	117.29	

^a Same as in Table IV.TABLE VII. Bond distances and angles for isolated thymine^a.

Distances (Å)	This work	Ref. 27	Exp.	Angles (deg)	This work	Ref. 27	Exp.
C4-N3	1.420	1.417	1.413	C4-N3-C2	128.46	128.17	126
N3-C2	1.399	1.393	1.345	N3-C2-N1	112.57	112.57	118
C2-N1	1.407	1.398	1.314	C2-N1-C6	123.77	123.70	123
N1-C6	1.386	1.387	1.408	N1-C6-C5	122.72	122.71	120
C6-C5	1.379	1.364	1.369	C6-C5-C4	118.10	118.12	119
C5-C4	1.481	1.470	1.476	C5-C4-N3	114.37	114.69	114
C5-CM	1.510	1.506	1.522	C4-C5-CM	118.03	117.97	119
C2-O2	1.235	1.233	1.246	N1-C2-O2	123.19	123.14	122
C4-O4	1.241	1.238	1.193	O4-C4-N3	120.35	120.07	121
N3-H3	1.028	1.025		C2-N3-H3	115.46	115.59	
N1-H1	1.024	1.022		C6-N1-H1	120.97	121.17	
C6-H6	1.097	1.096		C5-C6-H6	122.17	122.16	
CM-HM1	1.108	1.105		C5-CM-HM1	110.61	111.10	
CM-HM2	1.107	1.104		C5-CM-HM2	110.63	110.00	
CM-HM3	1.104	1.102		C5-CM-HM3	111.29	111.29	

^a Same as in Table IV.

TABLE VIII. H-bonds distances (in Å) and angles for SIESTA optimization of DNA base-pairs. D-A and D-H are the donor-acceptor and donor-hydrogen distances, respectively.

Pair	Bond	D-A	D-H	Angle
GCWC	N2(H)···O2	2.872	1.036	178.10
	N1(H)···N3	2.913	1.057	175.98
	O6···(H)N4	2.770	1.057	179.98
GG1	N1(H)···O6	2.755	1.057	174.67
	O6···(H)N1	2.756	1.057	174.59
GCNEW	N1(H)···O2	2.763	1.052	173.10
	O6···(H)N1	2.824	1.054	178.79
CC	N4(H)···N3	2.872	1.057	173.41
	N3···(H)N4	2.872	1.057	173.41
GG3	O6···(H)N2	3.169	1.026	167.00
	N7···(H)N1	2.864	1.043	171.91
GA1	N1···(H)N1	3.103	1.042	179.82
	N6(H)···O6	2.844	1.044	179.72
GT1	N1(H)···O4	2.797	1.048	179.40
	O6···(H)N3	2.839	1.058	175.18
GT2	O2···(H)N1	2.843	1.038	178.18
	N3(H)···O6	2.874	1.064	173.51
AC1	N3···(H)N6	3.007	1.039	173.69
	N4(H)···N1	3.046	1.044	176.89
GC1	N3···(H)N2	2.873	1.049	178.50
	N4(H)···N3	3.093	1.045	175.77
AC2	N6(H)···N3	2.957	1.041	169.11
	N7···(H)N4	2.994	1.048	177.18
GA3	N7···(H)N1	3.137	1.044	175.92
	N6(H)···O6	2.806	1.042	164.83
TAH	N3(H)···N7	2.828	1.066	175.94
	O4···(H)N6	2.991	1.035	170.84
TARH	O2···(H)N6	3.041	1.027	169.67
	N3(H)···N7	2.861	1.060	176.67
TAWC	N1···(H)N3	2.859	1.070	179.35
	N6(H)···O4	2.946	1.039	174.35
TARWC	N6(H)···O2	3.006	1.033	171.08
	N1···(H)N3	2.890	1.061	177.89
AA1	N1···(H)N6	3.049	1.041	177.53
	N6(H)···N1	3.049	1.041	177.53
GA4	N3···(H)N6	3.088	1.034	173.88
	N2(H)···N1	2.963	1.044	179.31
TC2	N3(H)···N3	3.065	1.053	168.05
	O4···(H)N4	2.822	1.041	176.27
TC1	N4(H)···O2	2.879	1.036	174.26
	N3···(H)N3	3.149	1.044	165.17
AA2	N7···(H)N6	3.051	1.037	176.28
	N6(H)···N1	3.062	1.040	166.63
TT2	N3(H)···O4	2.872	1.046	172.49
	O4···(H)N3	2.872	1.046	172.48
TT1	N3(H)···O4	2.885	1.049	169.12
	O2···(H)N3	2.876	1.050	170.11
TT3	N3(H)···O2	2.881	1.049	168.35
	O2···(H)N3	2.881	1.049	168.33
GA2	N6(H)···N3	3.146	1.027	166.86
	N7···(H)N2	3.006	1.040	173.24
GG4	N3···(H)N2	3.056	1.037	179.30
	N2(H)···N3	3.059	1.035	179.72
AA3	N7···(H)N6	3.070	1.031	159.56
	N6(H)···N7	3.070	1.031	159.57

2aminoAT	N6(H)···O6	2.921	1.034	176.95
	N3···(H)N1	2.955	1.069	178.95
	N2(H)···O4	2.998	1.027	176.27
GG2	O6···(H)N1	2.960	1.035	175.10
	N7···(H)N2	3.114	1.026	167.68
GC2	O2···(H)N1	2.917	1.040	174.15
	N3···(H)N2	3.139	1.027	177.41

TABLE IX. Relaxed Interaction and Stabilization Energies (kcal/mol) for the relaxed base-pair structures.

Base Pair	E_{int}	E_t
GCWC	-32.2	-27.6
GG1	-30.1	-26.7
GCNEW	-26.3	-19.6
CC	-21.1	-18.5
GG3	-18.2	-17.7
GA1	-17.9	-16.4
GT1	-18.9	-17.8
GT2	-17.8	-16.8
AC1	-16.4	-13.8
GC1	-18.0	-16.0
AC2	-17.9	-15.7
GA3	-16.5	-16.2
TAH	-17.6	-15.6
TARH	-16.4	-14.1
TAWC	-16.3	-14.2
TARWC	-15.1	-14.2
AA1	-14.2	-13.7
GA4	-14.2	-13.6
TC2	-13.8	-11.5
TC1	-12.2	-10.6
AA2	-13.7	-13.0
TT2	-13.1	-10.9
TT1	-12.9	-10.7
TT3	-12.6	-11.2
GA2	-12.9	-11.7
GG4	-9.6	-8.0
AA3	-11.6	-10.7
2aminoAT	-19.6	-16.8
GG2	-13.1	-12.4
GC2	-12.3	-10.2

TABLE X. Guanine-cytosine Watson-Crick base-pair^a.

	HF/6-31G**	DFT (B3LYP)	DFT (VWN-BP)	SIESTA
d(N2(H) ... O2)	3.017	2.930	2.930	2.872
d(N2,H)	1.001	–	1.035	1.035
d(N1(H) ... N3)	3.037	2.920	2.923	2.913
d(N1,H)	1.008	–	1.051	1.056
d(O6 ... H(N4))	2.921	2.780	2.785	2.770
d(H,N4)	1.007	–	1.055	1.057
E _{int}	-25.5	-29.6	-27.7	-32.2
E _T	–	-26.3	-22.9	-27.6

^a HF/6-31G**: results obtained at the HF level, with a 6-31G** basis. From ref. 21.

DFT (B3LYP): DFT results obtained with the Becke3LYP³⁹ functional. From ref. 21.

DFT (VWN-BP): DFT results obtained with the VWN⁴⁰ functional with BP⁴¹ non-local corrections. From ref. 27.

SIESTA: Present results.

TABLE XI. Thymine-adenine Watson-Crick base-pair^a.

	HF/6-31G**	DFT (VWN-BP)	SIESTA
d(N6(H) ... O4)	3.086	2.955	2.946
d(N6,H)	0.999	1.037	1.039
d(N1(H) ... N3)	2.988	2.66	2.859
d(N3,H)	1.013	1.067	1.070
E _{int}	-12.4	-13.9	-16.3
E _T	–	-11.9	-14.2

^a HF/6-31G**: results obtained at the HF level, with a 6-31G** basis. From ref. 21.

DFT (VWN-BP): DFT results obtained with the VWN⁴⁰ functional with BP⁴¹ non-local corrections. From ref. 27.

SIESTA: Present results.

TABLE XII. Cytosine-cytosine base-pair^a.

	HF/6-31G**	MP2//HF	MP2	DFT (B3LYP)	SIESTA
d(N4(H) ... N3)	3.050	3.050	2.980	2.900	2.872
E _{int}	-17.3	-18.8	-20.5	-20.4	-21.1
E _T	–	-17.5	-18.7	-18.1	-18.5

^a HF/6-31G**: results obtained at the HF level, with a 6-31G** basis. From ref. 21.

MP2//HF: results obtained at the MP2 level, with the HF geometries. From ref. 21.

MP2: results obtained at the MP2 level, with MP2 geometries. From ref. 21

DFT (B3LYP): DFT results obtained with the Becke3LYP³⁹ functional. From ref. 21.

SIESTA: Present results.